Polymer Properties
Quiz 12
April 26, 2019

We discussed osmotic pressure this week.

a) Consider that you put 1 gram of a material into 1000 ml of benzene, then fill one side of a container bisected by a semipermeable membrane with this solution and the other side with pure benzene. The solution side is 1 mm higher than the pure benzene side. The density of benzene is 0.876 g/cm^3 at room temperature (298K and R = 8.314 MPa cm^3/(K mole)) and the molecular weight of benzene is 78 g/mole. What is the molecular weight of the material you added? (g = 9.81m/s^2; MPa cm^3 = kg m^2/s^2)

b) For another solution you put in 10 grams of the same material into 1000 ml of benzene and repeat the measurement finding that the height of the pure benzene side is now 1.3 cm higher than the solution. Give the second virial coefficient B_2 and the second virial coefficient A_2. (Use the Flory Huggins equation for this analysis.)

c) You lower the temperature to 273K and the 10-gram solution is now 3 mm higher than the pure benzene. What can be done with this information? Could you identify the material from this information?

d) What would happen to the 1-gram solution if the temperature were dropped to 273K? What does it mean if this prediction is not correct?

e) How would these measurements and results be changed if the benzene at these temperatures was a good solvent? Could you measure the virial coefficient under that assumption?

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a) You need to assume an ideal solution since there is only one data point given and it seems to be fairly dilute. Part d can determine if this assumption is correct. For an ideal solution the osmotic pressure follows the ideal gas law:
$MW = cRT/\pi$
$\pi = \rho gh$ = (0.876 g/cm^3) (981 cm/s^2) (0.1 cm) = 85.9 g/(cm s^2) = 8.59 e^{-6} MPa
MW = 1e^{-2} g 8.314 MPa cm^3/(K mole) 298K/(8.59e^{-6} MPa) = 290,000 g/mole

b) For an ideal gas we expect the height to be 10 times part "a" but it is 13 times the height of "a". Since there is excess height over an ideal gas scaling, we expect that the solution will follow the virial expansion for the Flory-Huggins equation:
$\pi = RT(c/MW + c^2 A_2 + \ldots) = RT(n + n^2 B_2 + \ldots)$
$A_2 = (\pi/RT - c/MW)/(c^2)$
= {8.59 e^{-5} MPa/[8.314 MPa cm^3/(K mole) 298K] – 8.76 g/cm^3 /(290,000 g/mole)}/{8.76 g/cm^3}^{2}
$B_2 = MW^2 A_2$

c) $A_2 = a - b/T$ This can be used to predict the Boyle temperature where phase separation occurs. This could be used to identify the material since the phase separation point is fairly unique to a polymer/solvent pair as a function of molecular weight.

d) The height should drop to 1 mm 273K/298K = 0.916 mm if it is an ideal solution. If it is not correct then it is not dilute so you can't get the molecular weight in this way.

e) At low concentrations it is common to get the second virial coefficient for good solvents. At higher concentrations it is not possible.